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(84) **Blends of alkylene glycols and relatively high equivalent weight active hydrogen compounds containing multipurpose additives and process for preparing the same.**

(57) A compatibilized active hydrogen compound-alkylene glycol composition comprises components (A) a relatively high equivalent weight material having an average of at least about 1.8 active hydrogen containing groups per molecule and a weight from about 500 to about 5000 per active hydrogen containing group; (B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the composition; and (C) a compatibilizing and catalytic amount of an additive containing (1) a urea compound and (2) a transition metal salt of a carboxylic acid wherein said metal is selected from Groups I-B, II-B, V-A, IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table of the Elements; said composition containing a sufficient quantity of at least one amine group-containing material such that component (2) is soluble in said composition. Such compositions are useful in producing polyurethanes, particularly polyurethanes exhibiting relatively short demold times and good mold release properties. Unlike prior art compositions, the present compositions can generally be stored without substantial loss of activity.

**EP 0 416 399 A2**

# **BLENDS OF ALKYLENE GLYCOLS AND RELATIVELY HIGH EQUIVALENT WEIGHT ACTIVE HYDROGEN COMPOUNDS CONTAINING MULTIPURPOSE ADDITIVES AND PROCESS FOR PREPARING THE SAME**

This invention relates to polyurethanes and to compositions of relatively high equivalent weight active hydrogen compounds and alkylene glycols, said compositions containing materials that make the compositions useful in preparing polyurethanes.

In making polyurethanes, mixtures of a relatively high equivalent weight active hydrogen compound and a relatively low equivalent weight chain extender compound are reacted with a polyisocyanate. Using alkylene glycols as chain extenders often produces advantageous properties in resulting polyurethanes.

Alkylene glycol chain extenders are, however, often incompatible with relatively high equivalent weight active hydrogen compounds in amounts used to make polyurethane polymers. Therefore, the relatively high equivalent weight active hydrogen compound is often blended with the alkylene glycol just prior to use. Alternatively, an additional component which compatibilizes the alkylene glycol with the relatively high equivalent weight active hydrogen compound may be used. For instance, the use of urea and certain substituted ureas as compatibilizing agents is taught in U.S. Patents 4,485,031 and 4,485,032.

Use of compatibilizing agents is generally preferred because such use allows shipping and storage of blends of relatively high equivalent weight active hydrogen compounds and chain extenders. In many instances, the blends also contain other materials used in preparing polyurethanes, such as catalysts and certain additives. The reactivity of blends containing relatively high equivalent weight active hydrogen compounds, alkylene glycol chain extenders, compatibilizers having amine or urea functional groups and tin-containing catalysts such as certain dialkyl tin dicarboxylates, often diminishes during storage.

Some blends of polyether polyols and alkylene glycols compatibilized with ureas taught in U.S. Patent 4,485,032 show sufficient reactivity with isocyanates to form polyurethanes in the absence of tin carboxylate catalysts, but require 60 second demold times which exceeds the preferable demold times in automatic RIM processes.

Accordingly, it would be desirable to provide a compatibilized blend of relatively high equivalent weight active hydrogen compounds and glycol which blend contains materials having sufficient catalytic activity for polyurethane formation and exhibits relatively stable reactivity over time. It would also be desirable for the blend to have sufficient catalytic activity to produce polyurethanes which can be demolded in less than about 60 seconds. Preferably, the blend would also provide mold release properties for a polyurethane produced from the blend.

In one aspect, the invention is a compatibilized active hydrogen compound-alkylene glycol composition comprising components:

- (A) a relatively high equivalent weight active hydrogen compound material having an average of at least about 1.8 active hydrogen containing groups per molecule and an average molecular weight of from 500 to 5000 per active hydrogen containing group;
- (B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the composition; and
- (C) a compatibilizing and catalytic amount of an additive containing component (1) a urea compound and component (2) a transition metal salt of a carboxylic acid wherein said metal is selected from Groups I-B, II-B, V-A, IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table of the Elements; said composition containing a sufficient quantity of at least one amine group-containing material such that component (2) is soluble in said composition.

In other aspects, the invention includes polyurethane polymers prepared from the compositions of the invention and processes of preparing such polymers.

Compositions of the invention are compatibilized and additionally exhibit catalytic activity in forming polyurethanes. The catalytic activity is advantageously sufficient for use of the compositions in automatic RIM processes without additional catalyst. Additionally, polymers formed from the compositions of the invention exhibit self releasing characteristics.

One component of the composition of this invention is a relatively high equivalent weight active hydrogen compound. The term "relatively high equivalent weight" is used to refer to an equivalent weight (molecular weight per active hydrogen-containing group e.g. -OH, -NH<sub>2</sub>, -SH) of at least 500, preferably from 500 to 5000. The equivalent weight is preferably from 700 to 3000, and more preferably from 1000 to 2000. The relatively high equivalent weight active hydrogen compound also advantageously contains an average of at least 1.8, preferably from 1.8 to 6, more preferably from 2 to 3, nominal active hydrogen-containing groups per molecule. The active hydrogen groups are preferably hydroxyl groups, amine groups or mixtures thereof; more preferably hydroxyl groups.

Any suitable organic compound containing at least two active hydrogen containing groups as determined by the Zerewitinoff method may be used as an active hydrogen compound. Active hydrogen compounds are compounds having hydrogen containing functional groups which will react with an isocyanate group. The Zerewitinoff test described by Kohler in the Journal of the American Chemical Society, Vol. 49, page 3181 (1927) predicts the tendency of a hydrogen-containing group to react with isocyanates. Suitable active hydrogen compounds are those conventionally employed in the preparation of polyurethanes such as the compounds described in U.S. Patent 4,394,491, particularly in columns 3 through 5 thereof, wherein the compounds are called polyahls, which patent is incorporated herein by reference in its entirety.

Relatively high equivalent weight active hydrogen components most commonly used in polyurethane production are those compounds having at least two hydroxyl groups, which compounds are referred to as polyols. Representatives of the suitable polyols are generally known and are described in such publications as High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology" by Saunders and Frisch, Interscience Publishers, New York, Vol. I, pp. 32-42, 44-54 (1962) and Vol. II pp 5-6, 198-199 (1964); Kunststoff-Handbuch, Vol. VII, Vieweg-Hochtlen, Carl-Hanser-Verlag, Munich, pp. 45-71 (1966); and Organic Polymer Chemistry by K. J. Saunders, Chapman and Hall, London, pp. 323-325 (1973); and Developments in Polyurethanes, Vol 1, J. M. Buist, ed., Applied Science Publishers (1978) pp. 1-76.

Typical polyols include polyester polyols, polyester amide polyols, and polyether polyols having at least two hydroxyl groups. Polyethers and polyesters having hydroxyl-terminated chains are preferred for use as relatively high molecular weight active hydrogen containing compounds for use in polyurethanes suitable for use in the practice of the invention. Examples of polyols also include hydroxy functional acrylic polymers, hydroxyl-containing epoxy resins, polyhydroxy terminated polyurethane polymers, polyhydroxyl-containing phosphorus compounds and alkylene oxide adducts of polyhydric thioethers, including polythioethers, acetals, including polyacetals.

Polyether polyols are preferably employed in the practice of this invention because they are resistant to hydrolysis. Also, polyether polyols often exhibit incompatibility with alkylene glycols. Preferred among polyether polyols are polyalkylene polyether polyols including the polymerization products of oxiranes or other cyclic ethers such as tetramethylene oxide in the presence of such catalysts as boron trifluoride, potassium hydroxide, triethylamine and tributyl amine, or initiated by, for example, water, polyhydric alcohols having from two to eight hydroxyl groups and amines. Illustrative alcohols suitable for initiating formation of a polyalkylene polyether include ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,3-butylene glycol, 1,2-butylene glycol, 1,5-pentane diol, 1,7-heptane diol, glycerol, 1,1,1-trimethylolpropane, 1,1,1-trimethylolethane, hexane-1,2,6-triol, alpha-methyl glucoside, pentaerythritol, erythritol, pentatols and hexatols. Sugars such as, for example, glucose, sucrose, fructose and maltose, as well as compounds derived from phenols such as, for example, (4,4'-hydroxyphenyl)2,2-propane are also suitable polyhydric alcohols for forming polyether polyols useful in the practice of the invention.

The polyether is more preferably a polymer of one or more C<sub>2</sub>-C<sub>8</sub> cyclic ethers such as, for example, ethylene oxide, propylene oxide, butylene oxide, styrene oxide and tetrahydrofuran. Di- and/or trifunctional polymers of ethylene oxide and/or propylene oxide are preferred. The preferred polyethers are suitably block or random copolymers of propylene and ethylene oxide; but are more preferably block copolymers, most preferably block copolymers having ethylene oxide blocks at the termini of the polyethers such that there are primary hydroxyl groups on the polyethers. Such block copolymers are referred to as ethylene oxide capped polyols. The ethylene oxide caps preferably comprise at least about 10 weight percent of the polyol to produce high reactivity desirable for RIM processes.

Polyamines are also suitable for use as relatively high equivalent weight active hydrogen components in polyurethanes and include polyether polyamines; polyester polyamines; amine-functional polymers such as, for example, amine functional acrylates, amine terminated acetal resins, amine terminated urethanes, amine containing polyesters. Suitable amines include those having terminal primary or secondary aliphatic or aromatic amine groups, including those having terminal aromatic amine functionality such as, for example, p-amino phenoxy groups and p-amino m-methyl-N-phenyl carbamate groups. Compositions of amines with polyols are also suitably used as active hydrogen components. When amines are used as at least a portion of the active hydrogen component, polyurea and polyurea-urethane linkages are formed. Useful amines include polyoxyalkylene polyamines and cyanoalkylated polyoxyalkylene polyamines having equivalent weights of preferably from 500 to 10,000 and, more preferably, from 500 to 5000.

Among amines, amine-terminated polyethers are preferred for use in the practice of the invention. Amine-terminated polyethers are prepared from the polyether polyols described above by amination thereof. Amination is described in U.S. Patents 3,161,682; 3,231,619; 3,236,895; 3,436,359 and 3,654,370. For amination, it is generally desirable that the terminal hydroxyl groups in the polyol be essentially all

secondary hydroxyl groups for ease of amination. Secondary hydroxyl groups are introduced into a polyol produced from ethylene oxide by capping the polyol with higher alkylene oxides, that is, with alkylene oxides having more than two carbon atoms. Alternatively, secondary hydroxyl groups result from producing a polyol from higher alkylene oxides.

5 Generally, amination does not result in replacement of all the hydroxyl groups by amine groups. An aminated polyether polyol is selected to have a percentage of amine groups relative to hydroxy groups of from 0 to 100, preferably from 5 to 95 percent, depending on the physical properties desired in a resulting polyurethane. The amine groups are generally primary, but secondary amine groups may be formed. Beneficially, the amine-terminated polyols have an average functionality of from 2 to 6 amine groups per  
10 molecule. In the case of amines, the term "functionality" is used herein to refer to the number of amine groups, whether they be primary or secondary, in the molecule. Advantageously, the amine-terminated polyols have an average equivalent weight of at least about 500, preferably an average weight per active hydrogen-containing group of from 500 to 5000, more preferably from 500 to 2500. The process of utilizing aminated polyols disclosed in U.S. Patents 4,530,941 and 4,444,910 illustrate processes for using such  
15 compounds.

The composition also contains, as a chain extender, an alkylene glycol, preferably an  $\alpha,\omega$ -alkylene glycol, which is incompatible, in the absence of a compatibilizer, with the relatively high equivalent weight active hydrogen compound at the relative proportions thereof present in the composition. Suitable alkylene glycols include those having from 2 to 8, preferably from 2 to 6, more preferably from 2 to 4 carbon atoms  
20 because glycols with fewer carbon atoms, on reacting with a polyisocyanate, give rise to more crystalline hard segments. Exemplary chain extenders include ethylene glycol, 1,4-butanediol, 1,6-hexamethylene glycol and 1,8-octanediol. Ethylene glycol and 1,4-butanediol are most preferred.

Although the composition suitably contains any amount of glycol chain extender at which the chain extender and relatively high equivalent weight active hydrogen compound are incompatible in the absence  
25 of a stabilizer, the composition preferably contains from 5 to 60, more preferably from 10 to 40 parts by weight of chain extender per 100 parts by weight relatively high equivalent weight active hydrogen compound because vitrification is often observed when there is more than about 40 parts of glycol. It has been found that polyurethanes having particularly desirable properties may be prepared from blends containing an amount of chain extender within the preferred and more preferred ranges.

30 In addition to the relatively high equivalent weight active hydrogen compound and glycol chain extender, compositions of the invention preferably contain at least one amine. When the relatively high equivalent weight active hydrogen compound contains amine groups, and both compatibility of the glycol in the composition and solution of the transition metal carboxylate are achieved without an additional amine compound, the additional amine compound is not needed. Otherwise, an additional amine is needed. Use of  
35 an amine compound is especially preferred when there are more than about 10 parts by weight of glycol per hundred parts by weight relatively high equivalent weight compound and when a flexural modulus of at least about 5,000 psi is desired in a polyurethane prepared from the composition. Under certain circumstances the amine compound can additionally provide catalysis, chain extension, aid in mold release or other function. Exemplary of amines useful as chain extenders or cross-linking agents, for instance, are  
40 described in U.S. Patents 4,269,945; 4,433,067 and 4,444,910. Use as an active hydrogen component, for instance, is described in U.S. Patents 4,719,247 and 4,742,091. Use in an internal mold release composition, for instance, is described in U.S. Patent 4,585,803 and U.S. Patent 4,876,019.

Suitable amines which can be employed herein as a component in the composition of the invention include any aliphatic, cycloaliphatic, or aromatic compound containing at least one primary, secondary or  
45 tertiary amine group. The amines are, optionally, inertly substituted, that is, substituted with groups which do not undesirably interfere with the reactions of the amine group. Inert substitution includes, for instance, alkyl groups, cycloalkyl groups, aryl groups, arylalkyl groups, nitro groups, sulfate groups, sulfone groups, ether groups, hydroxyl groups, urethane groups and urea groups. Amines having alkyl, aryl, cycloalkyl, arylalkyl, ether, or hydroxyl groups are preferred.

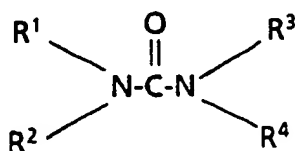
50 Preferred amines include unsubstituted or ether-substituted aliphatic or cycloaliphatic primary or secondary mono-amine compounds; trialkyl amines; hydroxyl amines, including alkyl diethanolamines, diethanolamine and dialkyl hydroxyl amines; tertiary amines such as those described by Nelson et al. in U.S. Patent 4,585,803 and low equivalent weight aliphatic and aromatic amine active hydrogen-containing compounds, such as amine-terminated polyethers of less than about 500, preferably from 200 to 500  
55 molecular weight, hexamethylene diamine, diethylenetriamine, and hydrocarbyl substituted aromatic amines such as, for example, diethylenetoluenediamine. An unsubstituted or ether-substituted aliphatic or cycloaliphatic primary mono-amine compound preferably contains from 4 to 8 carbon atoms. An unsubstituted or ether-substituted aliphatic or cycloaliphatic secondary mono-amine compound preferably con-

tains from 6 to 12 carbon atoms. An alkyl diethanol amine preferably has an alkyl group containing from 2 to 8 carbon atoms. A dialkyl hydroxyl amine preferably contains from 4 to 10 carbon atoms. In a trialkylamine, each alkyl group preferably has from about 2 to about 4 carbon atoms. Amines having these ranges of carbon atoms are preferred because these amines are effective compatibilizers. Amines described as useful with internal mold release agents in U.S. Patent 4,876,019 are particularly preferred because they are effective in achieving solutions of the internal mold release agents.

Suitable amines include, for example, oleyl amine, coco amine, tall oil amine, ethanolamine, diethyl-triamine, ethylenediamine, propanolamine, aniline and mixtures thereof. Other exemplary amines include n-butylamine, amylamine, n-hexylamine, n-octylamine, sec-butylamine, 1-amino-2-ethoxyethane, 1-amino-1-methyl hexane, cyclohexylamine, di-n-propylamine, ethylpropylamine, di-n-butylamine, di-n-hexylamine, di-sec-butylamine, ethyldiethanolamine, n-propyldiethanolamine, n-butyldiethanolamine, n-hexyldiethanolamine, diethylhydroxylamine, di-n-propylhydroxylamine, di-n-butylhydroxylamine, triethylamine, tri(n-propyl)amine, tri(n-butyl)amine, ethyl di(n-propyl)amine and diethanolamine. Suitable tertiary amines include, for example, triethylenedi-amine, N-methyl morpholine, N-ethyl morpholine, diethylethanolamine, N-coco morpholine, amino ethyl piperazine, 1-methyl-4-dimethyl-aminoethyl piperazine, 3-methoxy-N-dimethylpropylamine, N,N-diethyl-3-diethyl-aminopropylamine and dimethylbenzyl amine. Particularly suitable amines include aminated polyoxyalkylene glycols, hexamethylene diamine, diethylene triamine; and hydrocarbyl substituted aromatic amines such as diethylene toluene diamine.

The amount of amine present is not critical to this invention, but is advantageously determined by the purpose served by the amine in a given blend of alkylene glycol and relatively high equivalent weight active hydrogen compound. For instance, there is sufficient amine to compatibilize a mold release agent according to the teachings of U.S. Patent 4,876,019 or U.S. Patent 4,585,803. The invention is most useful in compositions containing sufficient amine to result in loss of activity of a tin-containing catalyst for the formation of polyurethanes. Preferably, at least about 0.1, more preferably from 0.05 to 4, most preferably from 0.2 to 1 part of amine is used per part of alkylene glycol chain extender because these amounts of amine aid in achieving compatibility of glycols in active hydrogen compounds using amounts of urea insufficient to result in gels in the active hydrogen composition. Most preferably, the composition contains from 0.5 to 20, even more preferably from 1 to 20 parts of the amine per 100 parts of relatively high equivalent weight active hydrogen compound because these amounts of amine are effective in preparing solutions of transition metal carboxylates.

Compositions of the invention additionally contain at least one urea compound, which is suitably (unsubstituted) urea or a substituted urea. A substituted urea advantageously is an inertly substituted urea, that is it has substitution which does not interfere undesirably with compatibilization of the composition or with catalysis of the polyurethane-forming reaction. Urea compounds used in the practice of the invention preferably are of Formula I:



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are inert substituents. Preferably, each of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently selected from hydrogen, alkyl groups, aryl groups, arylalkyl groups and cycloalkyl groups, which groups are unsubstituted or inertly substituted. The inert substituents on the groups include, for instance, ether groups such as alkoxy groups and aryloxy groups; fluorine, hydrogen, chlorine and hydroxy groups. The alkyl groups preferably have from 1 to 20, more preferably from 1 to 5 carbon atoms and include, for instance methyl, ethyl, propyl, hydroxymethyl and methoxypropyl groups. The aryl groups preferably have from 6 to 18, more preferably from 6 to 10 carbon atoms and include, for instance phenyl, p-fluorophenyl, 4-chlorophenyl and 4-methoxyphenyl groups. The alkyl aryl groups preferably have from 7 to 30, more preferably from 7 to 25 carbon atoms and include, for instance p-methyl phenyl and m-ethylphenyl. The arylalkyl groups preferably have from 7 to 10 carbon atoms and include, for instance benzyl and 2-phenyl-methyl groups. The cycloalkyl groups preferably have from 4 to 10 carbon atoms for instance cyclohexyl, methyl cyclohexyl and cyclobutyl groups. The alkoxy groups preferably have from 1 to 25 and include, for instance methoxy, ethoxy and propoxy. The aryloxy groups preferably have from 6 to 30, more preferably from 6 to 25 carbon atoms and include, for instance phenoxy and p-fluorophenoxy groups. Substituents having the indicated ranges of carbon atoms are preferred because they exhibit solubility as well as

combinations of catalytic and compatibilizing activity.

In Formula I, at least two of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are preferably hydrogen; more preferably, at least two of the hydrogen atoms are on the same carbon atom (e.g.  $R^1$  and  $R^2$  are both hydrogen). Most preferably, at least three, and even more preferably all 4 of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are hydrogen atoms to achieve maximum catalytic and compatibilizing efficiency. Preferred urea compounds include: urea, 1-methylurea, 1,1-diethyl urea. The most preferred compound is urea.

Additionally, there is at least one transition metal salt of a carboxylic acid (hereinafter transition metal carboxylate). The transition metal carboxylates are the salts of a metal cation from Groups IVB, VB, VIIB, VIII, IB, IIB and VA of the Periodic Table of the Elements with at least one carboxylate anion, that is the anion of an organic material having at least one carboxylic acid group. Although, all valences of the transition metals in the transition metal carboxylates are preferably filled with carboxylate anions; alternatively, the transition metal carboxylates include transition metal salts having metal-metal bonds or, preferably, ionic bonds to anions other than carboxylate anions, but not bonds directly to carbon as in alkylmetals. The transition metals include such metals as, for example, Ti, Zr, Ta, Cr, Mn, Mo, Fe, Co, Ni, Cu, Sb, Bi and Zn. Preferred metals are Zn, Cu, Sb, and Cd; more preferred, Sb, Cd and Zn; Zn, most preferred. These preferences are based on stability and reactivity under conditions present in polyurethane-forming processes. Suitable carboxylate anions include anions of saturated or unsaturated carboxylic acids having from 2 to 30, preferably from 8 to 21 carbon atoms, more preferably from 10 to 18 carbon atoms because these chain lengths are more effective in internal mold release. Suitable transition metal carboxylates include, for example, zinc stearate, zinc laurate, zinc myristate, copper stearate, copper laurate, copper oleate, copper palmitate, cadmium laurate, cadmium stearate, cadmium palmitate; antimony laurate, antimony stearate, nickel stearate, nickel oleate, nickel palmitate and nickel laurate. Particularly suitable are the zinc carboxylates which include, for example, zinc stearate, zinc oleate, zinc palmitate, zinc laurate, zinc stearyl sarcosinate, zinc oleoyl sarcosinate, zinc palmitoyl sarcosinate, zinc lauroyl sarcosinate; with zinc stearate, zinc laurate, and zinc myristate preferred; and zinc laurate, most preferred.

Together, the urea compound and transition metal carboxylate are present in amounts sufficient to catalyze reaction of the active hydrogen-containing components with a polyisocyanate and in amounts sufficient to compatibilize the relatively high equivalent weight active hydrogen compound and the alkylene glycol in the composition. The term "compatibilize" is used herein to denote that the composition remains in a single phase for at least 10 days of storage at a temperature of at least about 20° C.

The presence of sufficient urea compound and transition metal carboxylate to provide sufficient reactivity of the composition in polyurethane formation is indicated by formation of a gel which generally rapidly forms a hard polymer within at least about 40 seconds, preferably from 0.5 to 25 seconds, more preferably from 10 to 20 seconds from mixing of active hydrogen and polyisocyanate components. Preferably there is sufficient catalytic activity to provide sufficient reactivity to permit removal of a molded part from the mold in less than 60 seconds from the time components are injected into the mold (a 60 second demold time). The demold time is preferably from 1 to 30 seconds, more preferably from 1 to 20 seconds because these are the demold time found useful in automated RIM processes. In the case of integral skin foams, however, longer demold times, preferably less than about 2 minutes are suitable. Integral skin foams generally have interior densities of from 75 to 450, preferably from 150 to 350 Kg/m<sup>3</sup> (kilograms/cubic meter) whereas, other RIM produced polyurethanes generally have densities of from 600 to 1500, preferably from 900 to 1200 Kg/m<sup>3</sup>.

Preferably, the amounts of urea compound are sufficient to compatibilize the glycol and relatively high equivalent weight active hydrogen compound and preferably range from 1 part urea compound to 1 part glycol to 1 part urea compound to 15 parts glycol, more preferably from 1 part urea compound to 2 parts glycol to 1 part urea compound to 12 parts glycol, most preferably from 1 part urea compound to 3 parts of glycol to 1 part urea compound to 6 parts of glycol by weight. An excess of urea compound often results in formation of a gel in the active hydrogen composition, especially when urea rather than a substituted urea is used.

Preferably, from 0.1 to 10, more preferably from 0.5 to 5, most preferably from 1 to 3 parts by weight transition metal carboxylate per hundred parts by weight of the relatively high equivalent weight active hydrogen compounds are present. These ranges are preferred because, in the presence of the urea compounds, they provide sufficient reactivity of the composition.

The ratio of the urea compound to the transition metal carboxylate is preferably from 1:4 to 5:1, more preferably from 1:2 to 5:1 because these ratios provide sufficient reactivity and compatibility.

It is within the skill in the art to ascertain relative proportions of relatively high equivalent weight compound, alkylene glycol, urea compound, transition metal carboxylate and, optionally, amine useful in a specific application using the teachings herein. Amounts required for compatibilization and catalysis are



functions of characteristics of the composition such as the identity and amounts of components in the composition. For instance, when an amine present in the composition acts as a compatibilizer, the amount of urea compound needed for compatibilization is advantageously reduced. When another component, for instance, an amine has catalytic activity, relatively less urea compound and transition metal carboxylate are advantageously needed for catalysis.

The composition of this invention can be prepared by any admixing of the relatively high equivalent weight active hydrogen compound, glycol chain extender, urea compound and transition metal carboxylate that results in a homogeneous, compatibilized composition. Preferably, a first admixture of the urea and the glycol chain extender is formed, advantageously by shaking or stirring the materials together, advantageously at about room temperature. When an amine is used, a second admixture of the transition metal carboxylate and the amine is formed, advantageously by mixing them at a temperature of at least about 50°C until there is no visible evidence of two phases, preferably for about 30 minutes. The two admixtures are then combined with the relatively high equivalent weight compound and stirred using mild heat, e.g. about 35°C, if necessary to achieve a single phase. The alternative of solubilizing the urea compound or the carboxylate in the isocyanate compounds cannot, however, be dismissed.

In addition to the foregoing critical components, other additives which are useful in preparing polyurethanes may be present in the stabilized composition. Among these additives are, for example, catalysts, blowing agents, surfactants, crosslinkers, antioxidants, UV absorbers, preservatives, colorants, particulate fillers, reinforcing fibers, antistatic agents and internal mold release agents.

Suitable blowing agents, which are optionally employed herein, include, for example, water, halogenated methanes such as, for example, methylene chloride, dichlorodifluoromethane and trifluoromethane, the so-called "azo" blowing agents and finely divided solids. However, in preparing noncellular or microcellular polyurethanes, the use of these blowing agents is not preferred. In making microcellular polyurethanes having a density of from 600 to 1500 kg/m<sup>3</sup>, it is preferred to reduce density by dissolving or dispersing a gas such as dry air or nitrogen into the compatibilized composition prior to its reaction with a polyisocyanate.

Suitable surfactants include silicone surfactants and fatty acid salts, with the silicone surfactants being preferred. Such surfactants are advantageously employed in an amount of from 0.01 to 2 parts per 100 parts by weight relatively high equivalent weight active hydrogen compound.

Suitable fillers and colorants include, for example, calcium carbonate, alumina trihydrate, carbon black, titanium dioxide, iron oxide, flaked or milled glass, mica and talc. Suitable fibers include, for example, glass fibers, polyester fibers, graphite fibers and metallic fibers.

While additional catalysts for forming polyurethanes are, optionally, present in addition to the amine, urea and transition metal carboxylate in the compositions of the invention, additional catalysts are advantageously not necessary and, preferably, are not used. When additional catalysts are used, they are preferably catalysts which do not exhibit a substantial loss of activity when stored with other components of the compositions for times suitable for particular applications. More preferably, the catalysts lose less than about 50, most preferably less than about 25 percent of their reactivity (as measured by gel time) when stored with other components of a composition of the invention for a period of at least about 6 months at a temperature of at least about room temperature (e.g. 25°C). More preferably, tetravalent organometallic tin-containing catalysts which lose activity in the presence of amines, such as dialkyl tin dicarboxylates, tetraalkyl tins and tin oxides, particularly stannous oxide, are present in amounts insufficient to substantially increase the rate of polyurethane formation, (as measured by gel time). An increase of less than about 10 percent in gel time is considered insubstantial. Most preferably, there is less than about 0.001 weight percent tetravalent tin catalyst which loses activity in the presence of amines present in a composition of the invention. Specific catalysts are within the skill in the art and include those catalysts described, for instance, in U.S. Patent 4,269,945, particularly column 4, line 46 through column 5, line 25.

Active hydrogen component compositions of this invention are reacted with at least one polyisocyanate component to form a polyurethane. Both aliphatic and aromatic diisocyanates are useful for this purpose. Suitable aromatic diisocyanates include, for example, m-phenylene diisocyanate, p-phenylene diisocyanate, 2,4- and/or 2,6-toluene diisocyanate (TDI), naphthylene-1,5- diisocyanate, 1-methoxyphenyl-2,4-diisocyanate, 4,4'-biphenylenediisocyanate, 3,3'-dimethoxy-4,4'-biphenyldiisocyanate, 2,4'- and/or 4,4'-diphenylmethanediisocyanate (MDI) and derivatives thereof including polymeric derivatives. Preferred among the aromatic polyisocyanates are the isomers and derivatives of TDI and MDI.

Exemplary aliphatic polyisocyanates include isophorone diisocyanate, cyclohexane diisocyanate, hydrogenated diphenylmethanediisocyanate (H<sub>12</sub>MDI), 1,6-hexamethylenediisocyanate and the like. Of these, hexamethylenediisocyanate and H<sub>12</sub>MDI are most preferred.

Biuret, urethane, urea, uretonimine and/or carbodiimide containing derivatives, including prepolymers, of



the foregoing polyisocyanates are also suitable.

In preparing the polyurethane, the polyisocyanate is employed in an amount to provide from 0.9 to 1.5, preferably from 1.0 to 1.25, more preferably from 1.0 to 1.05, isocyanate groups per active hydrogen-containing group present in the reaction mixture. These ratios of isocyanate groups to active hydrogen-containing group are referred to herein as isocyanate index. Lesser amounts of polyisocyanate produce an inadequately cured polymer whereas greater amounts thereof tend to form undesirable crosslinking.

A composition of the invention is advantageously reacted with the polyisocyanate by forming a mixture therewith and introducing the mixture into a suitable mold for curing. Conventional casting techniques may be used, wherein the components are mixed and poured into the mold, where they cure upon heating. However, especially when more reactive components are used, it is preferred to conduct the reaction using a reaction injection molding (RIM) process. In such process, the components are subjected to high shear impingement mixing and immediately injected into a closed mold where curing takes place. In either the conventional casting or RIM techniques, in-mold curing takes place at least to an extent that the part retains its shape during demolding and subsequent handling. However, complete curing, i.e., curing to a point at which no additional discernable reaction occurs, may take place either in the mold or in a post-curing step which is conducted after demolding. In the practice of the invention, the postcuring step is preferably avoided. If needed, postcuring of the polyurethane is advantageously conducted at a temperature of about 250° F (121° C), but preferably less than about 350° F (177° C), for a period of from 1 minute to 24 hours, preferably from 1 minute to 3 hours because postcuring for these times produces polyurethanes having relatively better physical properties.

While the invention is useful in forming any polyurethane, particularly a molded polyurethane, it is particularly useful in the preparation of elastomeric polyurethanes using automated RIM processes. The invention is particularly important in producing high modulus RIM polyurethanes, preferably those having a flexural modulus greater than about 2,000 psi (14 MPa), more preferably greater than about 5,000 psi (35 MPa), most preferably greater than about 10,000 psi (70 MPa), and even more preferably greater than 20,000 psi (140 MPa) as measured by the procedure of ASTM D-747-86. Polyurethanes of the invention are often used to prepare automobile parts such as, for example, fascia, molded window gaskets, bumpers and steering wheels, as well as for non-automotive uses such as, for example, beer barrel skirts and shoe soles.

When polyurethanes prepared from the compositions of the invention are molded, particularly in a RIM process, they advantageously exhibit self release properties, that is, they release from a mold more easily than do polyurethanes containing the same other components, but not containing the combinations of urea and transition metal carboxylate of the invention.

The following examples are provided to illustrate the invention but are not intended to limit the scope thereof. All parts and percentages are by weight unless otherwise indicated. Examples (Ex.) of the invention are designated numerically, while Comparative Examples (C.E.), which are not examples of the invention, are designated alphabetically.

#### Examples 1-7: Catalytic Activity of Compositions Containing a Urea Compound, a Polyol, Ethylene Glycol, Zinc Laurate and an Amine

An admixture of 10 parts by weight ethylene glycol and 2 parts of the urea compound indicated in Table 1 was formed by stirring at room temperature. After about 30 minutes, 100 parts by weight of a 5000 molecular weight, glycerine-initiated poly(propylene oxide) which is ethylene oxide capped (hereinafter Polyol A) was added to the admixture and stirred for 15 minutes to form a first admixture. A second admixture of 2 parts by weight of zinc laurate with 7 parts by weight of difunctional, amine-terminated poly(propylene oxide) having an average molecular weight of about 400, commercially available from Texaco Chemical Corp. under the trade designation Jeffamine®D400 (hereinafter Amine A) was formed by stirring at about 65° C for 30 minutes.

For each of Examples 1-7, 112 parts by weight of the first admixture was mixed with 9 parts by weight of the second admixture by stirring for 10 minutes at a temperature of about 20° C to form a "B-Side" mixture. A sample of each "B-Side" mixture was thoroughly mixed within a sufficient sample of carbodiimide-modified diphenylmethanediisocyanate having an average equivalent weight of about 143 to produce a mixture having an isocyanate index of about 1.03.

The resulting mixture was quickly poured into a cup at room temperature, and the time from mixing the isocyanate and the "B-Side" mixture until a gel too stiff to stir manually was formed is recorded in Table I as the gel time.

For Comparative Examples A-G, the procedure of Examples 1-7 was followed omitting the zinc laurate

and Jeffamine®D400. Gel times are recorded in Table I.

A gel time of about 40 seconds or less is interpreted as indicating that the corresponding formulation is sufficiently reactive to be commercially useful in a high pressure automatic RIM process.

The data in Table I shows that, except when the urea is tetrasubstituted, formulations having polyol, glycol, urea compound, amine and zinc laurate in the "B-side" mixture exhibit sufficient reactivity to be useful in automatic RIM processes; whereas formulations not

TABLE I

Candidate Urea	Comparative Examples No.	Comparative Examples gel time (sec.)	Example No.	Examples (gel time) (sec)
Phenyl urea	A	100 + (no reaction)	1	Immediate reaction; semisolid at 59 sec..
1,1,Dimethyl urea	B	100 + (reacts slowly to a solid polymer)	2	Soft solid at 21 sec.
1-methyl urea	C	100 +	3	26
1,3,Dimethyl urea	D	100 +	4	37
1,1,3,3,tetramethyl urea	E	100 +	5	72
1,1,diethyl urea	F	100 +	6	26
Trimethylene Urea	G	100 +	7	40

having the amine and zinc laurate do not exhibit sufficient reactivity.

Example 8: Rim Process Using Formulation Containing Urea, Ethylene Glycol, Polyol, Amine, and Zinc Laurate and a Tin-Containing Catalyst

A first admixture was prepared by stirring 93 parts by weight of the Polyol A into a mixture of 10 parts of ethylene glycol and 2 parts of (unsubstituted) urea for about 10 minutes at 25° C. 150 grams of dibutyl tin dilauryl mercaptide commercially available from Witco Corp. under the trade designation UL-1 (Catalyst A) was mixed with the first admixture. A second admixture was prepared by stirring 7 parts by weight of the Amine A and 2 parts by weight of zinc laurate for about 30 minutes at a temperature of about 60° C. The first and second admixtures were combined by putting both into the B-side of an Admiral 2000 RIM machine and mixing by stirring and circulation. The polyisocyanate of Example 1 was placed in the A-side of the machine. The machine was calibrated to a 1.03 index (ratio of isocyanate groups to hydroxyl groups) by adjusting the machine to deliver the contents of the B- and A-sides at a weight ratio of 1.769 (B/A ratio).

The components were maintained at a temperature of about 80° F (27° C). A mixing pressure of about 2000 pounds per square inch (14,000 kPa) is used. The machine was adjusted for a shot time of about 1.3 seconds.

A plaque mold having an upper and a lower plate was used. The lower plate was stripped and polished before a very light coat of wax was applied. This plate was buffed after about each fourth plaque was produced; further buffing was unnecessary. The upper plate was waxed initially, but not additionally treated during the course of producing 20 plaques, all of which released easily from the mold.

The first 4 plaques were produced at a mold temperature of about 170° F (77° C). Then the mold temperature was reduced to about 160° F (71° C). Demold times were 15 seconds at 170° F (77° C) and 20 seconds at 160° F (71° C).

Example 9: RIM Process Using Formulation Containing Urea, Ethylene Glycol, Polyol, Amine, and Zinc Laurate

The process of Example 8 was repeated except that the tin-containing catalyst was omitted; the A-side was maintained at 100° F (38° C); the B-side was maintained at 110° F (43° C); the mold temperature was 165° F (74° C); the B/A ratio was 1.73; the demold time was 30 seconds. A light coat of wax was applied before molding begins. Seven plaques were produced which release easily from the mold.

The following physical properties of the polyurethanes formed in Examples 8 and 9 were measured according to the indicated ASTM procedures and are reported in Table II:

TABLE II

Example. No.	Ex. 8	Ex. 9
Polyol A	93	93
Amine A	7	7
Ethylene glycol	10	10
Urea	2	2
Zinc Laurate	2	2
Catalyst A	0.3	
Specific gravity <sup>(1)</sup>	0.8959	0.994
Flexural modulus <sup>(2)</sup> , psi, (MPa)	5106 (35)	5311 (37)
Tensile strength <sup>(3)</sup> , psi, (kPa)	1999 (14000)	2284 (16000)
Die C tear <sup>(4)</sup> , pli, (kN.m)	200 (35)	240 (42)
Elongation <sup>(5)</sup> %	260	245
Hardness <sup>(6)</sup> Shore A	86	85

<sup>(1)</sup>as measured by the procedure of ASTM D-792-86.

<sup>(2)</sup>as measured in pounds per square inch, psi (MPa) by the procedures of ASTM D-747-86.

<sup>(3)</sup>as measured in psi (kPa) by the procedures of ASTM D-638-84.

<sup>(4)</sup>as measured in pounds per linear inch, pli (kN.m) by the procedures of ASTM D-624-86.

<sup>(5)</sup>as measured in % by the procedures of ASTM D-638-84.

<sup>(6)</sup> as measured in Shore A by the procedures of ASTM D-2240-86.

The data in Table II show that polymers having good physical properties can be formed using compositions of the invention with or without additional catalyst. The compositions are sufficiently reactive without additional (tin-containing) catalyst to give demold times of 30 seconds. For comparison, it is noted that similar demold times cannot be achieved using similar compositions not containing conventional polyurethane formation catalysts from which either the urea or the zinc laurate is omitted. When tin catalyst is used with the zinc laurate and urea, the reaction is so fast that it is inconvenient for use in most commercial RIM processes.

#### Examples 10-13 and Comparative Example H: Variation of Urea Concentration

The procedure of Example 1 was repeated except that urea was used as the urea compound and the concentration of urea was varied as indicated in Table III. Observed gel times are recorded in Table III.

TABLE III

Example	Parts urea*	Gel Time in sec.
10	0.25	100 +
11	0.5	91 +
12	1.0	63
13	2.0	19

\* parts by weight per hundred parts polyol (Polyol A)

The data in Table III indicate that the reaction rate is dependent on the urea concentration. For comparison it is noted that much longer gel times are observed when secondary amines, such as cyclohexyl amine, are substituted for the urea and when the zinc laurate is omitted.

#### Example 14: Preparation of a High Modulus RIM Polymer

The process of Example 8 was repeated except that the tin-containing catalyst was omitted; the A-side and B-side compositions were maintained at 100° F (38° C); the mold temperature was 165° F (74° C); the B/A weight ratio was 1:1.21; the demold time was 30 seconds; the mixing pressure was 2,000 psi (14 MPa); the shot time was 1.5 sec.; the isocyanate was a hard segment methylenediphenyl-isocyanate prepolymer having an isocyanate equivalent weight of 170, commercially available from The Dow Chemical Company under the trade designation MDI Prepolymer 1288. A light coat of wax was applied before molding begins. Sixty plaques were produced which released easily from the mold, with no evidence of failure.

The following physical properties of the polyurethanes formed in were measured according to the indicated ASTM procedures given in Table II, except that Heat Sag was measured according to the procedure of ASTM D-3769-85; Gardner Impact at room temperature and -20° C were measured according to the procedure of ASTM D-3029-84 are reported in Table IV:

TABLE IV

	Example 14
Polyol A	93
Amyl amine	1
Amine A	7
Ethylene glycol	23.5
Zinc Laurate	2
urea	2
Specific gravity	0.996
Flexural modulus, psi (MPa)	83234 (574)
Tensile strength, psi (kPa)	3906 (27000)
Die C tear, pli (kN/m)	720 (126)
Heat Sag 4" (102 mm) overhang (mm)	9
Garner Impact at room temperature ft. lb. (m-kg)	>320 (>3.7)
Gardner Impact at -20° C ft. lb. (m-kg)	60 (0.69)
Elongation %	188
Hardness Shore D	64

The data in Table IV show that the compositions of this invention are suitable for use in preparing high modulus RIM polyurethanes having properties suitable for such applications as bumpers, facia, and automobile body panels.

#### Example 15: Preparation of an Integral Skin Foam Using a Blowing Agent

A first admixture was prepared by stirring 1 lb (454 g) urea and 8 lb (3632 g) of ethylene glycol; then adding 100 lb (45.4 kg) of Polyol A and 13 lb (5902 g) of trichlorofluoromethane, commercially available from DuPont de Nemours under the trade designation Freon 11 for about 10 minutes at 25° C. A second admixture of 2 lb (908 g) of zinc laurate, and 7 lb (3200 g) of Amine A was formed by heating to 65° C and stirring for about one hour. The first and second admixtures were combined and stirred at 25° C for 20 minutes. The resulting combination was placed in the "B-side" tank of an Admiral 2000 RIM machine. The isocyanate of Example 13 was placed in the "A-side" tank. The machine was operated under the following conditions:

component temperatures °F (°C)	80 (27)
Mixing pressure, psi (MPa)	2000 (14)
shot time, sec	1.0
through put, lb/sec (g/s)	3.0 (1360)
ratio of A to B side (1.05 index)	0.55
mold temperature °F (°C)	122 (50)

Fifty releases of plaques measuring 23.25 X 8.5 X 0.75 inches (5.9 m X 216 mm X 19 mm) were obtained after one treatment of a light spray coating of a wax mold release commercially available from Chem Trend Corporation under the trade designation Chem Trend RT-2002. By comparison, about one release was expected from the same treatment of a mold used to produce plaques of the same formulation but with a catalyst such as dimethyl tin dilaurate in place of the zinc laurate and urea in Example 15.

The properties of the integral foam were measured as in Example 14 and are reported in Table V:

TABLE V

	Example 15
density (kg/m <sup>3</sup> )	350
Tensile strength, psi (kPa)	351 (2420)
Die C tear pli (kN/m)	54 (9.45)
Elongation %	180

The data in Table V shows integral skin foams obtained in the practice of the invention have properties suitable for use in applications such as steering wheels, headrests and arm rests.

### Claims

1. A compatibilized active hydrogen compound-alkylene glycol composition comprising components:

(A) a relatively high equivalent weight active hydrogen compound having an average of at least about 1.8 active hydrogen containing groups per molecule and an average molecular weight of from 500 to 5000 per active hydrogen containing group;

(B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the composition; and

(C) a compatibilizing and catalytic amount of an additive containing (1) a urea compound and (2) a transition metal salt of a carboxylic acid wherein said metal is selected from Groups I-B, II-B, V-A, IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table of the Elements; said composition containing a sufficient quantity of at least one amine group-containing material such that component (2) is soluble in said composition.

2. A composition as claimed in Claim 1 wherein component (A) is at least one polyether polyol and wherein the composition contains an amine.

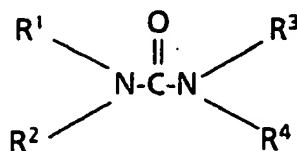
3. A composition as claimed in Claim 2 wherein the amine is an unsubstituted or ether-substituted aliphatic or cycloaliphatic primary or secondary mono-amine compound; a trialkyl amine; a hydroxyl amine; a tertiary amine; an amine terminated polyether having a molecular weight less than about 500, hexamethylene diamine, diethylenetriamine; a hydrocarbyl substituted aromatic amine; or a mixture thereof.

4. A composition as claimed in Claim 1 wherein the transition metal carboxylate salt has metal cat ion selected from Ti, Zr, Ta, Cr, Mn, Mo, Fe, Co, Ni, Cu, Sb, Bi, and Zn.

5. A composition as claimed in Claim 4 wherein the transition metal carboxylate salt has a carboxylate anion

having from 8 to 21 carbon atoms.

6. A composition as claimed in Claim 4 wherein the urea compound is represented by Formula I



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are inert substituents.

7. A composition as claimed in Claim 5 wherein the urea compound is urea.

8. A polyurethane polymer which is the reaction product of a polyisocyanate and the polyether-alkylene glycol composition of Claim 1.

9. A compatibilized active hydrogen compound-alkylene glycol composition comprising components (A) at least one relatively high equivalent weight active hydrogen compound; (B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the blend; and (C) a compatibilizing and catalytic amount of an additive containing (1) a urea compound and (2) a transition metal carboxylic acid salt; and (D) when component (A) does not have amine groups, at least one amine.

10. A composition as claimed in Claim 9 wherein component D is present in amounts of from 0.5 to 20 parts per hundred parts; component (2) is present in amounts of from 0.1 to 10 parts per hundred parts both based on parts by weight of the composition; and the weight ratio of component (1) to component (2) is from about 1:4 to about 5:1.

11. A polyurethane polymer prepared from a reaction mixture comprising an isocyanate component; a relatively high equivalent weight active hydrogen compound, an alkylene glycol which is incompatible with the active hydrogen compound at the relative proportions thereof present in the composition, an amine compound and a compatibilizing and catalytic amount of an additive containing (a) a urea compound and (b) a transition metal carboxylic acid salt.

12. A process for preparing a compatibilized active hydrogen compound-alkylene glycol composition which comprises admixing components:

(A) a relatively high equivalent weight active hydrogen compound having an average of at least about 1.8 active hydrogen containing groups per molecule and an average molecular weight of from 500 to 5000 per active hydrogen containing group;

(B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the composition; and

(C) a compatibilizing and catalytic amount of an additive containing (1) a urea compound and (2) a transition metal salt of a carboxylic acid wherein said metal is selected from Groups I-B, II-B, V-A, IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table of the Elements;

said composition containing a sufficient quantity of at least one amine group-containing material such that component (2) is soluble in said composition.





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⑳ Blends of alkylene glycols and relatively high equivalent weight active hydrogen compounds containing multipurpose additives and process for preparing the same.

㉑ A compatibilized active hydrogen compound-alkylene glycol composition comprises components (A) a relatively high equivalent weight material having an average of at least about 1.8 active hydrogen containing groups per molecule and a weight from about 500 to about 5000 per active hydrogen containing group; (B) an alkylene glycol which is incompatible with component (A) at the relative proportions thereof present in the composition; and (C) a compatibilizing and catalytic amount of an additive containing (1) a urea compound and (2) a transition metal salt of a carboxylic acid wherein said metal is selected from Groups I-B, II-B, V-A, IV-B, V-B, VI-B, VII-B or VIII of the Periodic Table of the Elements; said composition containing a sufficient quantity of at least one amine group-containing material such that component (2) is soluble in said composition. Such compositions are useful in producing polyurethanes, particularly polyurethanes exhibiting relatively short demold times and good mold release properties. Unlike prior art compositions, the present compositions can generally be stored without substantial loss of activity.

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# EUROPEAN SEARCH REPORT

Application Number

EP 90 11 6255

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-4 485 032 (F. OLSTOWSKI et al.) - - -		C 08 K 5/21 C 08 G 18/65 C 08 G 18/22 C 08 G 18/16
A	US-A-4 755 321 (C.T. MOSS et al.) - - -		
A	US-A-3 201 367 (K.L. SMITH) - - - - -		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 K C 08 G
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 06 March 91	Examiner VAN PUymbROECK M.A.
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